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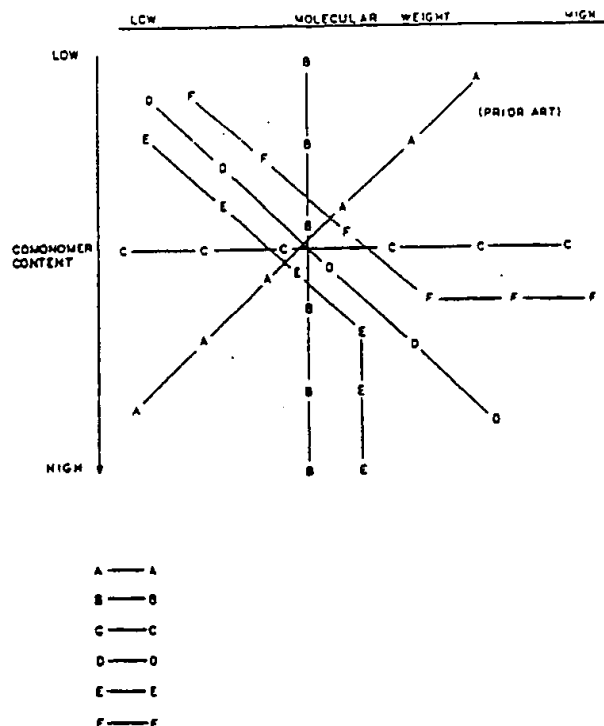
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(54) Title: LINEAR ETHYLENE INTERPOLYMER BLENDS OF INTERPOLYMERS HAVING NARROW MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS

(57) Abstract

Linear ethylene interpolymer blends are disclosed. The blends are made from components having a narrow molecular weight distribution (e.g. $M_w/M_n \leqslant 3$) and a narrow composition distribution (e.g. CDBI > 50 %). The blend components in a blend can all have the same molecular weight but different comonomer contents, the same comonomer content but different molecular weights, or comonomer contents which increase with molecular weight. The blends have either $M_w/M_n > 3$ or CDBI < 50 %, or both, and can be multimodal with respect to either or both molecular weight and/or comonomer content. The blends are generally free of blend components having both a higher average molecular weight and a lower average comonomer content than another blend component. The blends can have improved mechanical, physical and/or chemical properties.

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LINEAR ETHYLENE INTERPOLYMER BLENDS OF INTERPOLYMERS HAVING
NARROW MOLECULAR WEIGHT AND COMPOSITION DISTRIBUTIONS

SPECIFICATION

Field of the Invention

The present invention relates to polymer blends of
crystalline interpolymers, such as LLDPE, and more
particularly to blends of such interpolymers wherein each
5   blend component has a narrow molecular weight distribution
and a narrow composition distribution selected to obtain
superior properties in the blend.

Background of the Invention

Various types of polyethylene are known in the art.
10 Low density polyethylene ("LDPE") is generally prepared at
high pressure using free radical initiators and typically
has a density in the range of 0.915-0.940 g/cm^3. LDPE is
also known as "branched" polyethylene because of the
relatively large number of long chain branches extending
15 from the main polymer backbone.

High density polyethylene ("HDPE") usually has a
density in the range of greater than 0.940 to 0.960 g/cm^3.
HDPE is prepared using a coordination catalyst, e.g.
Ziegler-Natta type catalysts, at low or moderate
20 pressures, but sometimes at high pressure. HDPE is

generally linear without any substantial side chain branching. HDPE is a substantially crystalline polymer.

Linear, low density polyethylene ("LLDPE") is generally prepared in the same manner as HDPE, but

5   incorporates a relatively minor amount of an α-olefin comonomer such as butene, hexene or octene to introduce enough short chain branches into the otherwise linear polymer to reduce the density of the resultant polymer into the range of that of LDPE. The coordination

10   catalysts used to interpolymerize ethylene and the α-olefin generally produce an LLDPE with a relatively broad weight molecular weight distribution, i.e., Mw/Mn greater than about 3. Such LLDPE's also have relatively broad composition distribution in that the proportion of α-olefin

15   comonomer molecules incorporated into the polymer molecules varies. Generally, the lower molecular weight polymer molecules contain a relatively higher proportion of the α-olefin comonomer than the higher molecular weight polymer molecules.

20   A polyethylene such as LLDPE having a broad molecular weight distribution is undesirable in many respects, depending on the desired end use application. For example, LLDPE resins known in the prior art containing relatively high molecular weight molecules are subject to

25   orientation which results in anisotropic properties in the machine versus transverse direction of a fabrication process. On the other hand, resins containing relatively lower molecular weight molecules, in which the comonomer is invariably concentrated, tend to exhibit high block and

30   tackiness. These lower molecular weight, highly branched molecules interfere with the proper function of certain additives compounded in the resin, increase the percentage of extractable polymer, and increase fouling in the polymerization plant. The relatively high α-olefin

35   comonomer content of these low molecular weight polymer molecules causes such polymer molecules to be generally

amorphous and to exude to the surface of fabricated parts,
thereby producing an undesirable sticky surface.

5   Prior art polyethylenes such as LLDPE also generally
tend to have a very broad, nonuniform distribution of
comonomer content, i.e. some polymer molecules have a
relatively high α-olefin comonomer content while others
have a relatively low content. Generally, the polymer
molecules of low comonomer content are relatively more
crystalline and have a high melting temperature, whereas
10   the high comonomer content polymer molecules are more
amorphous and melt at a lower temperature. The presence
of a higher melting component is disadvantageous in many
applications, for example where softness or clarity is
desired. On the other hand, the presence of a lower
15   melting component frequently results in a high quantity of
extractables, which limit food contact applications.

Prior art blends of polyethylenes designed to improve
one or more of the properties of the blend relative to its
blend components or prior art polyethylene have also
20   suffered from the drawbacks mentioned above. For example,
incorporating a blend component with a high average
comonomer content to reduce crystallizability generally
results in an increase of extractables and adversely
affects other properties so that the full advantage of the
25   blend is not realized. Thus, there is a need to provide
ethylene interpolymer blends with superior properties and
in which the full advantages of blending may be realized.

Summary of the Invention

The present invention provides a blend of ethylene
30   interpolymer components with narrow molecular weight and
composition distributions selected to obtain an overall
molecular weight and composition distribution in the
resulting blend to impart superior properties thereto.
Broadly, the blends of this invention comprise a plurality
35   of linear ethylene interpolymer components wherein each
component has a M_w/M_n value less than or equal to 3 and a
composition distribution breadth index (as later

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described) of 50% or higher. The blend is substantially
free of blend components having both a higher average
molecular weight and a lower average comonomer content
than that of any other polyethylene component in the
5   blend. The components for the blend can be selected so
that the resultant blend has plural modality with respect
to molecular weight distribution, comonomer content, or
both.

In another aspect, the components for the blend are
10   linear ethylene interpolymers having the narrow molecular
weight and composition distributions mentioned above and
the blend components are selected from one of the groups
consisting of: (1) linear ethylene interpolymer blend
components having substantially the same average molecular
15   weight but different average comonomer contents; (2)
linear ethylene interpolymer blend components having
substantially the same average comonomer content but
different average molecular weights; and (3) linear
ethylene interpolymer blend components having different
20   average molecular weights and comonomer contents in which
the blend components, taken serially in order of
increasing average molecular weight, have an increasing
comonomer content.

In still another aspect, the linear ethylene
25   interpolymer blend components have the narrow molecular
weight and composition distribution mentioned above, and
for the linear ethylene interpolymer blend components
taken serially in order of increasing average molecular
weight, then each succeeding component has substantially
30   the same or a higher average comonomer content than each
preceding component in said series.

In another aspect, the invention provides a linear
ethylene interpolymer having plural modality with respect
to comonomer content, a narrow molecular weight
35   distribution such that $M_w/M_n \leq 3$ and an overall
composition distribution breadth index less than 50%.

In still another aspect, the invention provides a
linear ethylene interpolymer having plural modality with
respect to molecular weight so that the blend has broad
overall molecular weight distribution such that $M_w/M_n > 3$

5   and a composition distribution breadth index greater than
or equal to 50%.

In still another aspect, the invention provides a
linear ethylene interpolymer of plural modality with
respect to both comonomer content and molecular weight,

10 comprising a plurality of components having a narrow
molecular weight distribution such that $M_w/M_n \leq 3$ for each
fraction and each component taken serially in order of
increasing average molecular weight, has an increasing
average comonomer content.

15 In a still further aspect of the invention, there is
provided a linear ethylene interpolymer blend of plural
modality with respect to both comonomer content and
molecular weight which comprises a plurality of components
having a composition distribution breadth index of 50% or

20 more, wherein the components taken serially in order of
increasing comonomer content, have an increasing average
molecular weight.

Brief Description of the Drawings

Fig. 1 is a schematic illustration of different

25 blends made from poly(ethylene-co-α-olefin) blend
components having narrow molecular weight and composition
distributions.

Fig. 2 illustrates the broad molecular weight
distribution and broad composition distribution of a

30 typical prior art LLDPE.

Fig. 3 illustrates the narrow molecular weight
distribution and narrow composition distribution of an
exemplary blend component used in the present invention.

Fig. 4 illustrates the molecular weight distribution

35 and composition distribution of an exemplary LLDPE blend
according to an embodiment of the invention in which the

blend components have about the same molecular weight but
differing comonomer contents.

Fig. 5 illustrates the molecular weight distribution
and composition distribution of an exemplary LLDPE blend
5   according to another embodiment of the invention in which
the blend components have about the same comonomer content
but differing molecular weights.

Fig. 6 illustrates the molecular weight distribution
and composition distribution of an exemplary LLDPE blend
10   according to yet another embodiment of the invention in
which the conomoner contents of the blend components
increases as the molecular weight increases.

Description of the Preferred Embodiments

The linear ethylene interpolymer blend components in
15   the present invention are higher interpolymers of a major
proportion of ethylene and a minor proportion of
comonomer. The ethylene is generally polymerized in a
proportion of 70-100, typically 70-97, and often 70-80,
80-90 or 90-95, mole percent of the interpolymerized
20   monomers with 0-30, typically 3-30, and often 20-30, 10-20
or 5-10, mole percent comonomer. Contemplated blend
components generally include elastomer blend components in
the density range of about 0.85-0.900 g/cm^3, very low
density polyethylene blend components in the density range
25   of about 0.900-0.915 g/cm^3, and linear, low density
polyethylene blend components in the density range of
about 0.915-0.940 g/cm^3. Ethylene interpolymers having a
density in the high density polyethylene range above about
0.940 g/cm^3 are also contemplated as being suitably
30   employed in the invention.

Suitable comonomers interpolymerized with the
ethylene to obtain the ethylene interpolymer blend
components herein generally include monomers which may be
copolymerized with ethylene to obtain the molecular weight
35   distribution and comonomer distribution desired in the
blend component. A preferred class of comonomers are the

α-olefins having 3 to about 12 carbon atoms, such as
propylene, 1-butene, 1-pentene, 1-hexene,
3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene,
1-decene, 1-dodecane and the like. Other suitable
comonomers include vinyl cyclohexane, norbornene, vinyl
cyclohexene, and other diene comonomers such as
1,3-butadiene, 1,4-hexadiene, 4-methyl-1,4-hexadiene,
5-methyl-1,4-hexadiene, 1,5-hexadiene and the like. The
ethylene interpolymer may include one or more of such
comonomers, i.e. it may be a copolymer, terpolymer, etc.

The molecular weight of the LLDPE blend components
may range from one thousand to one million or more
depending on the particular end use, preferably 10^4-10^6,
and especially $2 \times 10^4 - 5 \times 10^5$. As used herein, the
terms "average molecular weight" and "molecular weight"
refer to weight average molecular weight unless otherwise
indicated. The linear polyethylene blend components
preferably have a narrow molecular weight distribution
(MWD). By "narrow MWD" is meant that the ratio of the
weight average molecular weight (M_w) to the number average
molecular weight (M_n) is less than or equal to 3.0.
Particularly preferred are the linear polyethylene blend
components having a very narrow MWD, i.e. M_w/M_n less than
or equal to 2.5, and especially less than or equal to 2.0.
Molecular weight distributions of ethylene interpolymers
are readily determined by techniques known in the art,
such as, for example, size exclusion chromatography.

The linear polyethylene blend components preferably
have a composition distribution (CD) such that the
composition distribution breadth index (CDBI) is at least
50%. The CDBI is defined as the weight percent of the
copolymer molecules having a comonomer content within 50
percent of the median total molar comonomer content. The
CDBI of linear polyethylene, which does not contain a
comonomer, is defined to be 100%. The CDBI of a copolymer
is readily calculated from data obtained from techniques
known in the art, such as, for example, temperature rising

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elution fractionation as described, for example, in U.S. Patent Application Serial No. 151,350 or in Wild et al., J. Poly. Sci, Poly. Phys. Ed., vol. 20, p. 441 (1982). Unless otherwise indicated, terms such as "comonomer
5   content", "average comonomer content" and the like refer to the bulk comonomer content of the indicated interpolymer blend, blend component or fraction on a molar basis.

A graphical illustration of an exemplary narrow MWD,
10 narrow CD blend component is seen in Fig. 3. In this three-dimensional figure, the Y-axis is the molecular weight, the X-axis is the molar comonomer content, and the Z-axis represents the incidence or weight proportion of molecules. As can be seen, the MWD and the CD of the
15 blend component are narrow and appear as relatively sharp peaks in Fig. 3. In contrast, the MWD/CD diagram for a typical conventional LLDPE seen in Fig. 2 shows a broad MWD and a broad CD, and the comonomer content tends to decrease as the molecular weight increases.

20   In the blends of the present invention, one or more of the properties of the blend are improved by appropriate selection of narrow MWD, narrow CD blend components. In one embodiment, for example, tear strength may be controlled by blending linear polyethylene resins having
25 about the same average molecular weight but with different average comonomer contents. Such a blend is illustrated as line B in Fig. 1. In another embodiment, the comonomer contents of the linear polyethylene blend components are the same, but molecular weights are varied, as illustrated
30 by line C in Fig. 1. In still further embodiments illustrated by lines D, E and F in Fig. 1, the blend components taken serially in order of increasing molecular weight, or in order of increasing molar comonomer content, have the same or higher comonomer content or molecular
35 weight, respectively.

As used herein, two or more blend components have substantially the same molecular weight if the resulting

MWD of the blend thereof is similarly narrow to the MWD of each blend component, i.e. the value of M_w/M_n of the resulting blend is less than or equal to about 3.0, preferably less than about 2.5. Conversely, two or more

5   blend components have a different average molecular weight if the overall M_w/M_n of the resulting blend is relatively greater than for each such blend component, i.e., the M_w/M_n of the blend is greater than 3.0. As used herein, two or more blend components have a different comonomer

10   content if the overall CDBI of the resulting blend is relatively less than that of each such blend component, i.e., the overall CDBI of the blend is less than 50%. Conversely, two or more blend components have substantially the same molar comonomer content if the

15   resulting CD of the blend thereof is similarly narrow with respect to each blend component, i.e., the resulting blend has a CDBI of 50% or greater. It is readily appreciated that the CD and MWD of a blend can depend on the relative proportions of each blend component employed therein.

20   It is specifically contemplated that blend components may have the "same" molecular weight for purposes of one blend, but not for the purpose of another blend, e.g. wherein the components would result in the blend having an MWD less than or greater than 3.0 depending on the

25   proportion of each blend component. Similarly, blend components may have a "different" comonomer content for purposes of one blend, but not for the purposes of another blend, e.g. wherein the components would result in the final blend having CDBI less than or greater than 50%

30   depending on the proportion of each blend component.

The molecular weight and composition distribution of a bimodal blend of the invention is illustrated graphically in Fig. 4. It is seen from this MWD/CD diagram that the comonomer content of each of the blend

35   components is different, while the molecular weight of each blend component is about the same. This blend corresponds to line B of Fig. 1. In contrast, a similar

graph for typical conventional LLDPE is seen in Fig. 2,
and line A of Fig. 1, and shows that the lower molecular
weight fractions contain more of the comonomer than the
higher molecular weight fractions. The lower molecular
5   weight molecules which contain relatively high comonomer
concentrations as in this conventional LLDPE can cause
undesirable effects such as poor surface properties, high
block and tackiness, cling development, high levels of
extractables, and fouling of polymerization plants. In
10   the present invention, such effects are minimized and
properties are enhanced by providing blends of the type
illustrated in Curve B, C, D, E, and F.

As an example of the embodiment of Curve B, it has
been found that a 50-50 blend of a first LLDPE having a
15   6.4 mole% 1-butene content and a M_w of 80,400 (M_w/M_n = 2.3;
CDBI = ~67%; MI 4.0 dg/min; density 0.9042 g/cm^3) with a
HDPE having a 0.0 mole% 1-butene content and a M_w of
76,700 (M_w/M_n = 2.8; CDBI = ~100%; MI 5.0 dg/min; density
0.9552 g/cm^3) has an Elmendorf tear strength of 210 g/mil,
20   synergistically enhanced in contrast to the tear strengths
of 111 and 48 g/mil for the respective first and second
blend components. Further, a 25-75 blend of these same
components has a further enhanced Elmendorf tear strength
of 227 g/mil. This result is quite surprising and
25   unexpected because including a higher proportion of the
second LLDPE resin with the lower tear strength in the
blend increases the tear strength of the resulting blend,
rather than decreasing the tear strength as would be
expected.
30   In another embodiment exemplified in Fig. 5 and line
C of Fig. 1, a multimodal MWD is obtained by blending
linear polyethylene components having narrow molecular
weight and composition distributions, and about the same
comonomer content, but differing molecular weights. The
35   molecular weight distribution of such blends improves the
melt processability and rheological characteristics
thereof, for example, high extrusion rates, high bubble

stability, high shear sensitivity, reduced draw resonance. On the other hand, the optical properties of mechanical, surface and individual blend components are generally substantially retained or improved in the blend thereof,

5 including, for example tear strength, modulus, yield strength, reduced blocking, clarity, gloss, haze and the like. Moreover, such blends have lower portions of soluble molecules than prior art copolymers having similar molecular weight distribution. Desirable molecular weight

10 and composition distributions may be obtained by blending different components, or by polymerization of the blend components simultaneously in the same reactor or in multiple reactors.

The higher molecular weight fraction containing

15 relatively less comonomer as in conventional LLDPE may cause an anisotropic morphology during fabrication processing known as "row nucleated" or "shish-ka-bob" morphology. This anisotropic morphology is believed to contribute to poor toughness in articles crystallized from

20 flowing melts. In the present invention, the anisotropy may be minimized by providing a blend with lower concentrations of such higher molecular weight molecules with a relatively low comonomer content and by incorporating the comonomer in the blend components as

25 indicated in blend B, C, D, E and F.

In another embodiment as exemplified by Fig. 5 and line D of Fig. 1, the blend includes components having narrow molecular weight and composition distributions, but differing average molecular weights and average comonomer

30 contents. However, in contrast to conventional LLDPE as illustrated in line A of Fig. 1 and in Fig. 2, the blend of this embodiment has a greater comonomer content in the higher molecular weight fractions or blend components than in the lower molecular weight fractions or blend

35 components. These distributions are obtained, for example, by blending narrow MWD, narrow CD linear polyethylene resins which, taken serially in order of

increasing molecular weight, have an increasing comonomer
content.   It is also contemplated that the blend may
include two or more blend components having the same
molecular weight as illustrated by line F in Fig. 1, in
5   which case such components would be included in the serial
ordering secondarily in order of their increasing average
comonomer content. Also, the presence of two or more
blend components having the same comonomer content is also
contemplated as being within the purview of this
10   embodiment, as illustrated by line E in Fig. 1, provided
that there is included either at least one blend component
having a higher comonomer content and molecular weight or
at least one blend component having a lower comonomer
content and lower molecular weight than any of the blend
15   components having the same comonomer content. In this
embodiment, the blend is preferably substantially free of
blend components having both a higher molecular weight and
a lower comonomer content than any component present in
the blend.

20   Such a blend has properties which are significantly
different from prior art blends and conventional LLDPE
resins in which the comonomer content generally decreases
in proportion to increasing molecular weight components or
fractions. The isotropy and toughness of films made from
25   such blends are improved by minimizing the anisotropic
shish-ka-bob or row-nucleated morphology ordinarily caused
by a low concentration of comonomers present in the higher
molecular weight molecules in conventional LLDPE resins.
Moreover, such blends have desirable properties such as,
30   for example, reduced blocking, reduced coefficients of
friction, and lower extractables, in comparison to
conventional LLDPE resins.

     The linear polyethylene blend components of the
invention may be prepared by use of catalyst systems of
35   the metallocene type known to provide narrow CD/MWD
resins. Cyclopentadienylide catalyst systems using a
metallocene complex in conjunction with an alumoxane

cocatalyst or reaction product thereof are suitable for
preparing the polymer components utilized in the blends of
the invention. The metallocene catalyst may be
represented by the general formula $(C_p)_m MR_n R'_p$ wherein C_p

5   is a substituted or unsubstituted cyclopentadienyl ring; M
is a Group IVB, or VB transition metal; R and R' are
independently selected halogen, hydrocarbyl group, or
hydrocarboxyl groups having 1-20 carbon atoms; m = 1-3,
n = 0-3, p = 0-3, and the sum of m + n + p equals the

10 oxidation state of M. Various forms of the catalyst
system of the metallocene type may be used for
polymerization to prepare the polymer components of the
present invention including those of the homogenous or the
heterogeneous, supported catalyst type wherein the

15 catalyst and alumoxane cocatalyst are together supported
or reacted together onto an inert support for
polymerization by gas-phase, high pressure, slurry, or
solution polymerization.

The cyclopentadienyls of the catalyst may be

20 unsubstituted or substituted with hydrogen or hydrocarbyl
radicals. The hydrocarbyl radicals may include alkyl,
alkenyl, aryl, alkylaryl, arylalkyl, and like radicals
containing from about 1-20 carbon atoms or where 2 carbon
atoms of cyclopentadienyl are joined together to form a

25 C_4-C_6 ring. Exemplary hydrocarbyl radicals include
methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl,
isobutyl, heptyl, octyl, nonyl, decyl, cetyl,
2-ethylhexyl, phenyl and the like. Exemplary halogen
substituents include chlorine, bromine, flourine and

30 iodine. Of these halogen atoms, chlorine is preferred.
Exemplary hydrocarboxy radicals are methoxy, ethoxy,
propoxy, butoxy, amyloxy and the like. Illustrative, but
non-limiting examples of the metallocene catalyst useful
in preparing the polymers of the present invention include

35 bis(cyclopentadienyl)titanium dimethyl,
bis(cyclopentadienyl)titanium diphenyl,

bis(cyclopentadienyl)zirconium dimethyl,
bis(cyclopentadienyl)zirconium diphenyl,
bis(cyclopentadienyl)hafnium dimethyl and diphenyl,
bis(cyclopentadienyl)titanium di-neopentyl,

5   bis(cyclopentadienyl)zirconium di-neopentyl,
bis(cyclopentadienyl)titanium dibenzyl,
bis(cyclopentadienyl)zirconium dibenzyl,
bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl
metallocenes such as bis(cyclopentadienyl)titanium methyl

10   chloride, bis(cyclopentadienyl)titanium ethyl chloride,
bis(cyclopentadienyl)titanium phenyl chloride,
bis(cyclopentadienyl)zirconium methyl chloride,
bis(cyclopentadienyl)zirconium ethyl chloride,
bis(cyclopentadienyl)zirconium phenyl chloride,

15   bis(cyclopentadienyl)titanium methyl bromide,
bis(cyclopentadienyl)titanium methyl iodide,
bis(cyclopentadienyl)titanium ethyl bromide,
bis(cyclopentadienyl)titanium ethyl iodide,
bis(cyclopentadienyl)titanium phenyl bromide,

20   bis(cyclopentadienyl)titanium phenyl iodide,
bis(cyclopentadienyl)zirconium methyl bromide,
bis(cyclopentadienyl)zirconium methyl iodide,
bis(cyclopentadienyl)zirconium ethyl bromide,
bis(cyclopentadienyl)zirconium ethyl iodide,

25   bis(cyclopentadienyl)zirconium phenyl bromide,
bis(cyclopentadienyl)zirconium phenyl iodide; the trialkyl
metallocenes such as cyclopentadienyltitanium trimethyl,
cyclopentadienyl zirconium triphenyl, and cyclopentadienyl
zirconium   trineopentyl,   cyclopentadienylzirconium

30   trimethyl, cyclopentadienylhafnium triphenyl,
cyclopentadienylhafnium trineopentyl, and
cyclopentadienylhafnium trimethyl.

Other metallocenes which may be usefully employed to
prepare the polymer components of the invention include

35   the monocyclopentadienyls titanocenes such as,
pentamethylcyclopentadienyl titanium trichloride,

pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH_2 and derivatives of this

5 reagent such as bis(cyclopentadienyl)Ti=CH_2.Al(CH_3)$_3$, (Cp_2TiCH_2)$_2$, $Cp_2TiCH_2CH(CH_3)CH_2$, $Cp_2Ti-CHCH_2CH_2$; substituted bis(cyclopentadienyl)titanium (IV) compounds such as: bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides;

10 dialkyl, trialkyl, tetra-alkyl and penta-alkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride and other dihalide complexes;

15 silicon, phosphine, amine or carbon bridged cyclopentadiene complexes, such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl

20 or dichloride and other dihalide complexes and the like.

Additional zirconocene catalysts useful according to the present invention include bis(cyclopentadienyl) zirconium dimethyl; bis(cyclopentadienyl) zirconium dichloride, bis(cyclopentadienyl) zirconium

25 methylchloride, pentamethylcyclopentadienyl zirconium trichloride, pentaethylcyclopentadienyl zirconium trichloride, bis(pentamethylcyclopentadienyl)zirconium diphenyl, the alkyl substituted cyclopentadienes, such as bis(ethylcyclopentadienyl)zirconium dimethyl,

30 bis(β-phenylpropylcyclopentadienyl)zirconium dimethyl, bis(methylcyclopentadienyl)zirconium dimethyl, bis(n-butyl-cyclopentadienyl)zirconium dimethyl, bis(cyclohexylmethylcyclopentadienyl)zirconium dimethyl, bis(n-octyl-cyclopentadienyl)zirconium dimethyl, and

35 haloalkyl and dihalide complexes of the above; di-alkyl, trialkyl, tetra-alkyl, and penta-alkyl cyclopentadienes, such as bis(pentamethylcyclopentadienyl)zirconium

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di-methyl,   bis(1,2-dimethylcyclopentadienyl)zirconium
dimethyl and dihalide complexes of the above; silicon,
phosphorus, and carbon bridged cyclopentadiene complexes
such as dimethylsilyldicyclopentadienyl zirconium dimethyl
5   or dihalide, and methylene dicyclopentadienyl zirconium
dimethyl or dihalide, and methylene dicyclopentadienyl
ethylene bridged bis(tetrahydroindenyl) zirconium dimethyl
or dihalide, carbenes represented by the formula
$Cp_2Zr=CHP(C_6H_5)_2CH_3$, and derivatives of these compounds
10   such as $Cp_2\overline{ZrCH_2CH(CH_3)CH_2}$.

Bis(cyclopentadienyl)hafnium dichloride,
bis(cyclopentadienyl)vanadium dichloride and the like are
illustrative of other metallocenes.

The alumoxanes are polymeric aluminum compounds which
15   can be represented by the general formulae $(R-Al-O)_n$ which
is a cyclic compound and $R(R-Al-O-)_nAlR_2$, which is a
linear compound. In the general formula R is a C_1-C_5
alkyl group such as, for example, methyl, ethyl, propyl,
butyl and pentyl and n is an integer from 2 to about 20.
20   Generally, in the preparation of alumoxanes from, for
example, aluminum trimethyl and water, a mixture of the
linear and cyclic compounds is obtained.

The alumoxane can be prepared in various ways.
Preferably, they are prepared by contacting water with a
25   solution of aluminum trialkyl, such as, for example,
aluminum trimethyl, in a suitable organic solvent such as
benzene or an aliphatic hydrocarbon. For example, the
aluminum alkyl is treated with water in the form of a
moist solvent. In an alternative method, the aluminum
30   alkyl such as aluminum trimethyl can be desirably
contacted with a hydrated salt such as hydrated copper
sulfate.

Preferably, the alumoxane is prepared in the presence
of a hydrated ferrous sulfate as described in U.S. Patent
35   4,665,208. The method comprises treating a dilute
solution of aluminum trimethyl in, for example, toluene,
with ferrous sulfate represented by the general formula

$FeSO_4 \cdot 7H_2O$. The ratio of ferrous sulfate to aluminum trimethyl is desirably about 1 mole of ferrous sulfate for 6 to 7 moles of aluminum trimethyl. The reaction is evidenced by the evolution of methane.

5   The ratio of aluminum in the alumoxane to total metal in the metallocenes can be in the range of about 0.5:1 to about 10,000:1, and preferably about 5:1 to about 1000:1.

      Various inorganic oxide supports may be used for supported catalyst systems to prepare interpolymers and
10   blend components of the present invention. The polymerization is generally carried out in the temperature range of about 0-160°C, or even higher, but this range is not meant to be exclusive for preparing the interpolymer and blend components of the invention, which may be
15   prepared by any technique resulting in the structure set forth. Atmospheric, sub-atmospheric, or super-atmospheric pressure conditions have been used for the polymerization using the metallocene catalyst described above. It is generally preferred to use catalyst compositions at a
20   concentration so as to provide from about 1 ppm to about 5000 ppm, most preferably 10 ppm to 300 ppm, by weight of transition metal based on the weight of monomers in the polymerization of the ethylene polymers.

      A slurry polymerization process generally uses
25   super-atmospheric pressures and temperatures in the range of 40-110°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid
30   employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or toluene is
35   employed.

      In a modification, the polymer components of the present invention may be formed by gas-phase

polymerization. A gas-phase process utilizes super-atmospheric pressure and temperatures in the range of about 50°-120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and

5   product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a

10   temperature of 50°-120°C. Triethylaluminum may be added as needed as a scavenger of water, oxygen, and other adventitious impurities. Polymer product can be withdrawn continuously or semi-continuously at a rate such as to maintain a constant product inventory in the reactor.

15   After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without

20   further deactivation or catalyst removal. The polymer obtained can be extruded into water and cut into pellets or other suitable comminuted shapes. Pigments, antioxidants and other additives may be added to the polymer, as is known in the art.

25   The blends of the present invention are prepared by blending the desired components in the desired proportions using conventional blending, techniques and apparatus, such as, for example, screw-type extruders, Banbury mixers, and the like. Alternatively, the blends may be

30   made by direct polymerization, without isolation of the blend components, using, for example, two or more catalysts in one reactor, or by using a single catalyst and two or more reactors in series or parallel. The blend may also be compounded with various conventional additives

35   known in the art such as, for example, antioxidants, UV stabilizers, pigments, fillers, slip additives, block additives, and the like. The blend preferably does not

contain any blend components in proportions which would significantly adversely affect any improved properties desired to be obtained by blending the LLDPE resins.

The invention is illustrated by way of the following

5   examples:

Example 1

An ethylene homopolymer resin, identified as '006, having characteristics shown in Table 1, was prepared in a gas phase reactor employing a silica supported transition

10   metal catalyst described below.

The gas phase reaction was carried out at 185°F reaction temperature, 195 psi ethylene pressure, a hydrogen/ethylene mole ratio of 0.00041, and a residence time of 2 hours. A second polymer, an ethylene/butene-1

15   copolymer identified as '013, having characteristics shown in Table 1 was prepared in the gas phase reactor using the same supported catalyst as described below. The gas phase reaction was carried out at 140°F reactor temperature, 195 psi ethylene pressure, a hydrogen/ethylene mole ratio of

20   0.00061, a butene-1/ethylene mole ratio of 0.123, and a residence time of 2 hours.

The silica supported transition metal catalyst was obtained as follows:

100 grams of high surface area (Davison 952) silica,

25   dehydrated in a flow of dry nitrogen at 800°C for 5 hours, was slurried with 500 cc of toluene at 25°C under nitrogen in a 2500 cc round-bottom flask using a magnetic stirrer. 250 cc of methyl alumoxane in toluene (1.03 mole/liter in aluminum) was added dropwise over 15 minutes with constant

30   stirring to the silica slurry. Stirring was continued for 30 minutes while maintaining the temperature at 25°C. To the alumoxane treated silica slurry was added dropwise over 15 minutes, with constant stirring 250.0 cc of toluene solution containing 2.00 grams of

35   bis(n-butylcyclopentadienyl)zirconium dichloride. This slurry was stirred an additional one half hour while maintaining the temperature at 65°C and thereafter the

toluene was decanted and the solids recovered and dried in
vacuo for 4 hours. Analysis of the catalyst indicated
that it contained 4.5 wt% aluminum and 0.63 wt% zirconium.

5   Resins '006 and '013 were then intensively mixed at
360°F in equal proportions in a Banbury melt blender along
with 1000 ppm each of the stabilizers Irganox 1076 and
Irgafos 168. The molten blend from the Banbury was
transferred to a roll mill, made into a thin sheet and
then cooled to room temperature. The cold sheet was then
10   chopped into approximately 1/8 inch chips.
Characteristics of this blend, identified as Blend B1, are
given in Table 1.

          Compression molded sheets, five thousandth of an inch
in thickness, were prepared by melting the chopped blend
15   at 160°C in a press, compressing to 20 tons pressure for 5
minutes and then cooling the blend under pressure to room
temperature at a rate of 15°C per minute. Properties of
the molded sheet specimen are shown in Table 2.

          Example 2
20   A second compression molded sheet was prepared and
tested as in Example 1, from the resins described in
Example 1, except that the blend which is identified as
Blend B2, consisted of one part '006 and three parts '013.
Characteristics of Blend B2 are given in Table 1,
25   properties of Blend B2 are given in Table 2.

TABLE 1
POLYMER CHARACTERIZATION

Sample Designation	Mole% Butene[a]	M_w[b]	M_w/M_n[b]	Density[c]	Melt Index[d]	CDBI[e]
'006	0.0%	76,700	2.8	0.9552	5.0	100%
'013	6.4	80,400	2.3	0.9042	4.0	67%
Blend B1	2.7	76,500	2.4	0.9335	4.4	25%
Blend B2	4.9	76,900	2.3	0.9172	4.3	44%

a. By C-13 NMR
35   b. Weight average molecular weight (M_w), and ratio of number average
     molecular weight (M_n), M_w/M_n by size exclusion chromatography.

c. Density by gradient column method, ASTM D1585, g/cm^3
d. Melt index by ASTM D1738 Condition E, dg/min
e. CDBI, composition distribution breadth index, is defined as the weight
   percent of polymer molecules having a comonomer content within 50% of the
5   median total molar comonomer content CDBI; of HDPE is defined to be
   100%. Determined using temperature rising elution fractionation
   using tetra-chloroethylene solvent over a 6°C to 120°C temperature range
   as described in U.S. Patent Application Serial Number 151,350.
   See also Wild, et al, _J. Poly. Sci. Ed_, Vol. 20, p 441 (1982).

10

TABLE 2
TEAR AND TENSILE STRENGTH OF MOLDED SHEET

Sample Designation	Tear Strength[e]	Tensile Strength[f] @ Yield	Tensile Strength[f] @ Break	Elongation[f] @ Yield	Elongation[f] @ Break	Modulus[f] Secant	Modulus[f] Tangent
'006	48	3640 psi	840	18%	710%	127,000	155,000
'013	111	800	3230	70	1830	165,000	---
Blend B1	210	1900	2870	23	1620	70,600	76,000
Blend B2	227	1330	3030	28	1530	37,700	42,000

e. Tear strength, in g/mil, measured using ASTM 1922, tear resistance
   by pendulum method
20 f. Tensile strength, elongation, and modulus measured using ASTM D638

Example 3

Polymers used as blend components were synthesized by
a procedure similar to that described below for Run 03. A
stainless steel, 1-liter Zipperclave autoclave reactor was
25 used in the syntheses. The reactor was equipped with a
water jacket for heating and cooling, a septum inlet for
injection of liquid components, a burette for measuring
and adding purified hexane, and a controlled pressure
source of purified ethylene and nitrogen. Polymerization
30 reactions were started by cleaning the reactor and purging
it with purified nitrogen for several hours. 800 cc of
purified hexane was added to the reactor vessel at 25°C by
means of the measuring burette. 100 cc of purified
1-hexene was then added under nitrogen, and the contents
35 of the reactor were continuously stirred at 1200rpm
henceforth. 10.0 cc of the 10 wt% solution of
methylalumnoxane was added by syringe, and the reactor
temperature was equilibrated at the reaction temperature
of 60°C. Hydrogen was not used in this example

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it is added at this time in the examples which do use it.
Hydrogen was metered into the reactor from a vessel of
known volume equipped with a highly precise pressure
gauge. The ideal gas law was used to calculate the
5   millimoles of hydrogen introduced into the reactor.
1.00 cc   of   a   solution   of   0.01 wt%
bis(n-butylcyclopentadienyl) zirconium dichloride in
distilled toluene was then injected by syringe, followed
by pressurization immediately with 90.9 psi of purified
10   ethylene. Ethylene was fed continuously on demand to the
stirring   reactor   while   maintaining   the   reaction
temperature at 60°C and the reaction pressure at 90 psi.
After 10 minutes of polymerization the reaction was
stopped by rapidly cooling and venting the pressure and
15   exposing the contents to air. The polymer was obtained by
evaporating the liquid components and drying in a vacuum
oven for 1 hour. The poly(ethylene-co-hexene-1) polymer
obtained, which is identified as CO3, was obtained in 89.7
yield.
20   Other polymerizations runs were performed using the
procedure above with the exception that the volumes,
temperatures, and other polymerization conditions were
modified as shown in Table 3. Characterization data for
the blend components are given in Table 4.
25   Blends 8A, 9D, 20C, 21F and 22E were each prepared
using equal quantities of three blend components. (The
letter designation in these blends corresponds to the type
of blend illustrated in Figure 1.) Blend components for
each of the blends are given in Table 4, and they were
30   blended by the following solution blending procedure using
ca. 14 g. of each blend component. 2000 cc of xylene was
purged with nitrogen for one hour, the three blend
components were added, and the mixture was stirred and
heated to 144°C to dissolve the polymers. The polymer
35   solution was then cooled to 70°C, and 2000 cc of methanol
was added to precipitate the polymer. The mixture was
then cooled to 22°C, and the precipitated polymer was

filtered and dried in a vacuum oven. Average composition,
composition distribution breadth index, molecular weight
data, and density of the blends are listed in Table 4.

Compression molded sheets, five thousandth of an inch

5   in, thickness, were prepared by melting the blended
polymers in a press, compressing to 20 tons pressure for 5
minutes and then cooling the blend under pressure to room
temperature. Properties of the molded sheet specimen are
shown in Table 5 for blends 8A, 9D, 20C, 21F and 22E. The

10   fraction of polymer extracted by hexane at 69°C is also
given for the blends.

Table 5 shows that the tear strength of blends 9D,
20C, 21F and 22E, i.e., blends having novel
composition-molecular weight distributions, are each

15   superior to that of blend 8A, which has a
conventional-type composition-molecular weight
distribution. In many applications it is desirable to
have low levels of extractable polymer, and the table
shows that blends 9D, 20C, 21F, and 22E are markedly

20   superior to blend 8A in this respect. Moreover, tensile
properties such as tensile strength at yield of the
conventional-type blend 8A are generally comparable to the
tensile strengths of the other blends. Consequently, the
benefits of high tear strength and low levels of

25   extractables can be achieved without undue loss of tensile
properties.

This example illustrates the benefits obtained by
certain novel composition-molecular weight distributions
differing from the conventional type. Thus, blends 9D and

30   20C have similar average molecular weights and molecular
weight distributions. Consequently, flow and melt
fabrication performance of these blends should be similar
to that of the conventional-type blend 8A. Therefore, the
desirable mechanical and solubility properties of blends

35   9D and 20C are not obtained at the expense of fabrication
performance. Additionally, blends 21F and 22E have much
lower weight average molecular weight than blend 8A, and

they should therefore be more easily fabricated into articles of commerce such as films, fibers and molded objects.

In summary, in the blends of this example (Type C, D, E and F blends) the average molecular weight and molecular weight distribution can be manipulated independently of the composition distribution. Superior solid state performance can therefore be achieved without sacrificing melt fabrication performance.

TABLE 3
POLYMERIZATION CONDITIONS

Polymeri-zation Run No.	Reaction Temp.°C	$C_2^=$ Press. (psi)	Time (min.)	Hexane (cc)	1-Hexene (cc)	Catalyst Solu. (cc)	Yield gm	H_2 m mole
03	60	90	10	800	100	1.0	89.7	--
09	80	60	10	800	75	1.0	36.6	--
15	80	60	15	800	--	1.0	47.0	10
19	80	60	60	800	75	0.25	44.2	5
27	90	60	45	800	150	0.50	96.5	--
30	75	75	42	800	87.5	0.55	86.3	--
38	60	130	20	800	150	0.20	89.5	--
42	60	60	30	800	--	1.0	81.0	--
48	70	170	9	300	600	0.5	114.0	--
64	68	302	60	--	800	0.05	53.0	--

TABLE 4

POLYMER CHARACTERIZATION OF BLENDS AND BLEND COMPONENTS

	Sample[(h)] Designation	Mole %[(a)] Hexene	Mw[(b)]	Mw/Mn[(b)]	Density[(b)]	CDBI[(b)]
5	C27	6.1	12,500	1.9	--	77%
	C30	2.0	48,800	1.9	--	81
	C42	0.0	259,000	2.0	--	100
	Blend 8A[(c)]	2.7	113,000	9.0	0.933	24
	C15	0.0	13,400	2.7	--	100
10	C30	2.0	48,000	1.9	--	81
	C64	4.2	223,000	2.2	--	--
	Blend 9D[(d)]	2.1	95,600	9.8	0.940	42
	C19	2.3	13,600	1.9	--	70
	C30	2.0	48,800	1.9	--	81
15	C38	2.2	240,000	2.2	--	--
	Blend 20C[(e)]	2.3	94,800	8.8	0.932	64
	C15	0.0	13,400	2.7	--	100
	C09	3.0	52,000	2.4	--	79
	C03	3.1	121,000	2.2	--	67
20	Blend 21F[(f)]	--	62,000	6.4	0.946	46
	C15	0.0	13,400	2.7	--	100
	C09	3.0	52,000	2.4	--	79
	C48	7.2	50,000	1.9	--	75
	Blend 22E[(g)]	--	37,800	4.2	0.940	37

25   (a) Calculated from absorbance of 1378 cm^{-1} IR band using spectral substraction to correct for overlap of adjacent IR bands. Residual peak at 1378 cm^{-1} was converted to hexene content using calibration obtained by C13 NMR analysis of poly(ethylene-co-hexenes).

30   (b) Same as in Table 1

       (c) Blend 8A consisted of equal quantities of C27, C30 and C42

       (d) Blend 9D consisted of equal quantities of C15, C30 and C64

       (e) Blend 20C consisted of equal quantities of C19, C30 and C38

       (f) Blend 21F consisted of equal quantities of C15, C09 and C03

35   (g) Blend 22E consisted of equal quantities of C15, C09 and C48

       (h) Blend components in this table are identified by the letter C followed by the corresponding polymerization run number from Table 3. For example, blend component C27 was obtained from polymerization run 27.

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TABLE 5
PROPERTIES OF MOLDED SHEET

Sample	Tear Strength g/mil	Tensile Strength at Yield, psi	Hexane Extractable Polymer %
Blend 8A	68	1770	22
Blend 9D	241	1980	3.0
Blend 20C	426	1400	6.3
Blend 21F	205	2050	4.5
Blend 22E	107	2050	6.7

(a) Tear strength measured by ASTM 1922, tear resistance by pendulum method.

(b) Tensile strength at yield measured using ASTM D638.

(c) Extractables were determined as follows. About 0.5 g of polymer molded sheet, ca. 5 mil thick, was weighed and placed in a weighed cellulose extraction thimble. The thimble and polymer were placed in a vapor jacketed Soxlet-type extractor, and the polymer was extracted with condensed vapors of boiling hexane at 69°C for 16 hours. The thimble and residual polymer were removed, dried in a vacuum oven, and weighed to determine the amount of extracted, i.e., soluble, polymer.

The foregoing description of the invention is illustrative and explanatory thereof. Various changes in the materials, apparatus, and particular steps employed will occur to those skilled in the art. It is intended that all such variations within the scope and spirit of the appended claims be embraced thereby.

CLAIMS:

1   1.   A polymer blend, comprising:
2   a plurality of linear ethylene interpolymer
3   blend components, each having a narrow molecular weight
4   distribution such that $M_w/M_n \leq 3$ and a composition
5   distribution breadth index of at least 50%;
6   wherein the blend is essentially free of blend
7   components having both a higher average molecular weight
8   and a lower average comonomer content than that of any
9   other said polyethylene blend component; and
10   wherein the blend has either $M_w/M_n > 3$ or a
11   composition distribution breadth index below 50%, or both.

1   2.   The blend of claim 1, wherein said blend has a
2   density in the range of 0.85 to 0.94 g/cm^3.

1   3.   The blend of claim 1, wherein said blend
2   components have an α-olefin comonomer content in the range
3   of 0 to 30 mole percent and an ethylene content in the
4   range of 100 to 70 mole percent.

1   4.   The blend of claim 1, wherein said blend
2   components are selected from the group consisting of:
3   poly(ethylene-co-α-olefin) elastomers; very low
4   density linear polyethylenes; and linear, low density
5   polyethylenes.

1   5.   The blend of claim 1, wherein the blend
2   components have essentially the same molecular weight and
3   different comonomer contents.

1   6.   The blend of claim 1, wherein the blend
2   components have essentially the same comonomer content and
3   different molecular weights.

1   7.   The blend of claim 1, wherein the molecular

2 weights and the comonomer contents of the blend components

3 are both different.

1   8.   The blend of claim 1, wherein the value of M_w/M_n

2 for each blend component is less than or equal to 2.5.

1   9.   The blend of claim 1, wherein the composition

2 distribution breadth index for each blend component is

3 greater than about 70%.

1   10. A polymer blend, comprising:

2   a plurality of linear ethylene polymer or

3 interpolymer blend components, each having a narrow

4 molecular weight distribution such that $M_w/M_n \leq 3$ and a

5 composition distribution breadth index of at least 50%;

6 and

7   wherein said blend components are selected from

8 one of the groups consisting of: (1) blend components

9 having essentially the same average molecular weight but

10 different average comonomer contents; (2) blend components

11 having essentially the same average comonomer content but

12 different average molecular weights; and (3) blend

13 components having different average molecular weights and

14 comonomer contents wherein said components, taken serially

15 in order of increasing average molecular weight, have an

16 increasing comonomer content.

1   11. The blend of claim 10, wherein the blend has a

2 density of 0.85 to 0.94 g/cm^3.

1   12. The blend of claim 10, wherein said blend has an

2 average molar α-olefin comonomer content of 1-30 percent.

1   13. The blend of claim 10, wherein said blend

2 components include poly(ethylene-co-α-olefin) elastomers.

1   14.   The blend of claim 12, wherein said blend
2   components include very low density, linear polyethylenes.

1   15.   The blend of claim 12, wherein said blend
2   components include linear, low density polyethylenes.

1   16.   The blend of claim 10, wherein the number of
2   said blend components is from 2 to 5.

1   17.   The blend of claim 10, wherein said blend is
2   essentially free of blend components having both a higher
3   average molecular and a lower average comonomer content
4   than another blend component.

1   18.   The blend of claim 10, wherein the blend has
2   plural   modality   with   respect   to   molecular   weight,
3   comonomer content or both.

1   19.   The blend of claim 12, wherein said α-olefins
2   have from 3 to about 12 carbon atoms.

1   20.   The blend of claim 10, wherein $M_w/M_n \leq 2.5$ for
2   each blend component, and the composition distribution
3   breadth index for each component is in the range from 50
4   to 70%.

1   21.   The blend of claim 20, wherein $M_w/M_n \leq 2.0$ for
2   each blend component.

1   22.   The blend of claim 20, wherein each blend
2   component has a composition distribution breadth index in
3   the range from 50 to 90%.

1   23.   A   polymer   blend   exhibiting   enhanced   tear
2   strength properties over that of the individual blend
3   components comprising:
4   a plurality of linear ethylene interpolymer
5   blend components, each having a narrow molecular weight
6   distribution   such   that $M_w/M_n \leq 3$ and   a   composition
7   distribution breadth index of at least 50%; and
8   wherein for said components taken serially,
9   primarily in order of increasing molecular weight and
10 secondarily in order, of increasing average comonomer
11 content, each succeeding component has substantially the
12 same or a higher average comonomer content than each
13 preceding component in said series.

1   24.   A polymer blend of linear ethylene interpolymer
2   having a molecular weight distribution such that $M_w/M_n > 2$
3   and a composition distribution breadth index greater than
4   or equal to 50%.

1   25.   A   linear   ethylene   interpolymer   comprising
2   fractions having a narrow molecular weight distribution
3   such that $M_w/M_n \leq 3$ for each fraction, said fractions
4   taken serially in order of increasing average molecular
5   weight have an increasing average comonomer content.

1   26.   A   linear   ethylene   interpolymer   comprising
2   fractions having a composition distribution breadth index
3   of 50% or more, said fractions taken serially in order of
4   increasing comonomer content have an increasing average
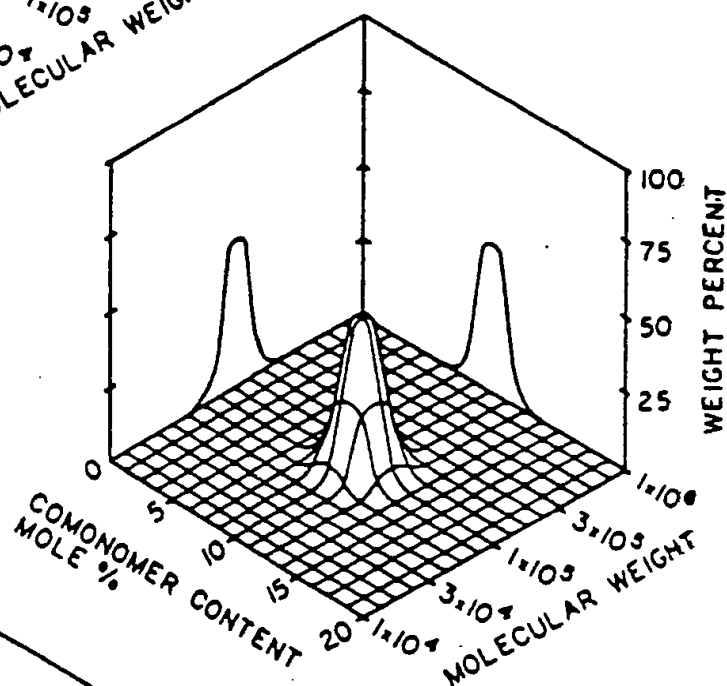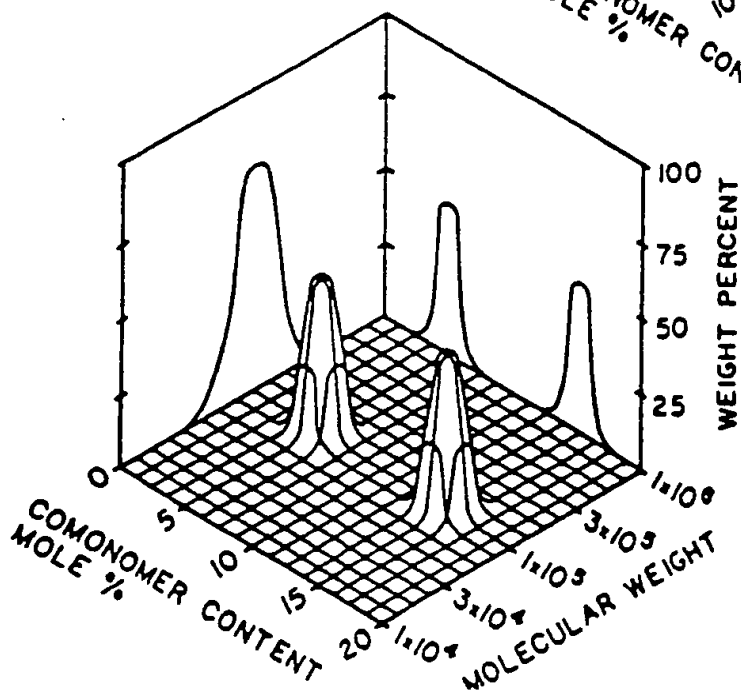5   molecular weight.
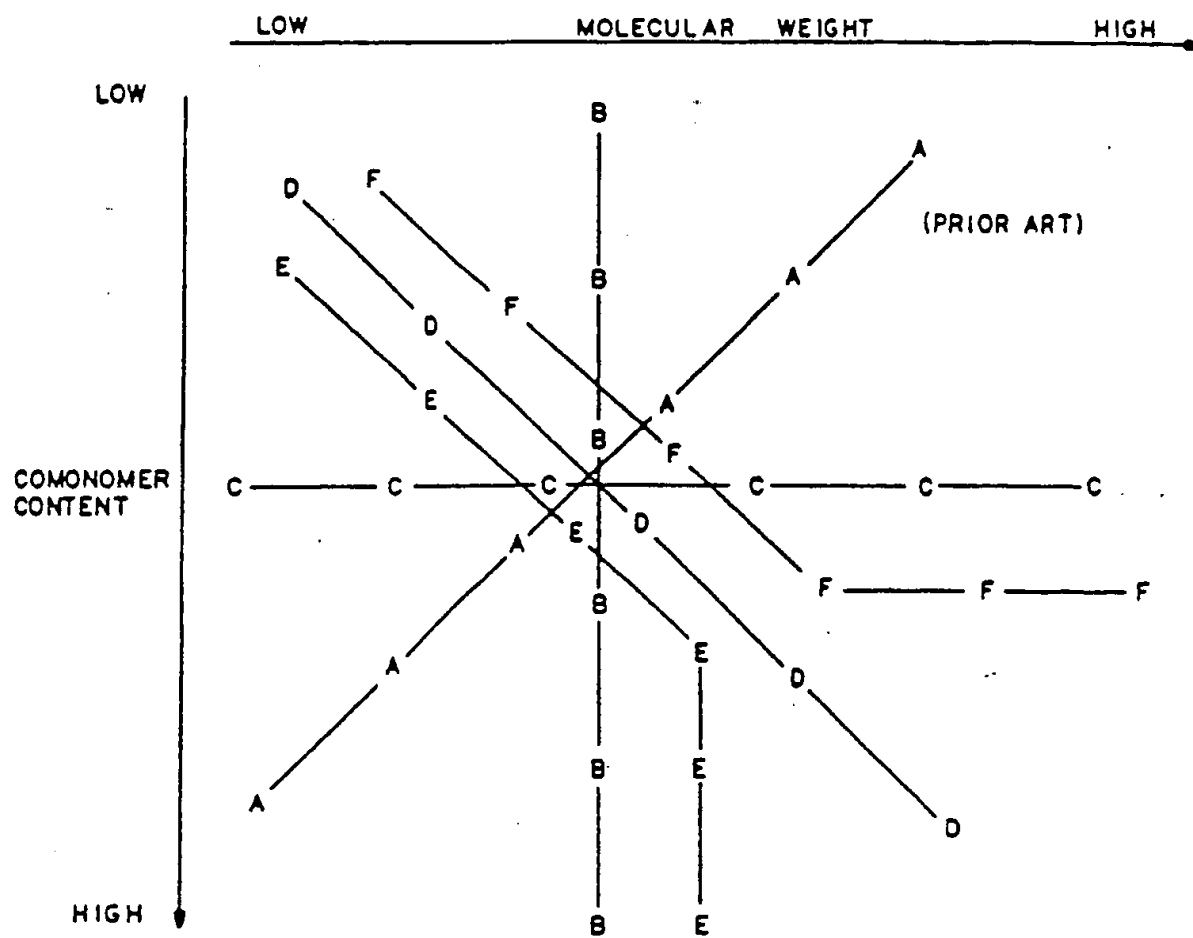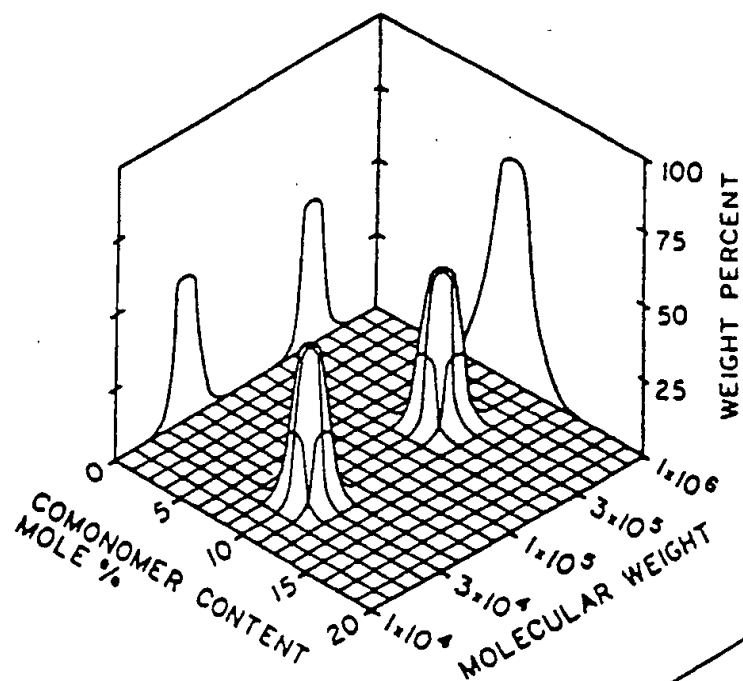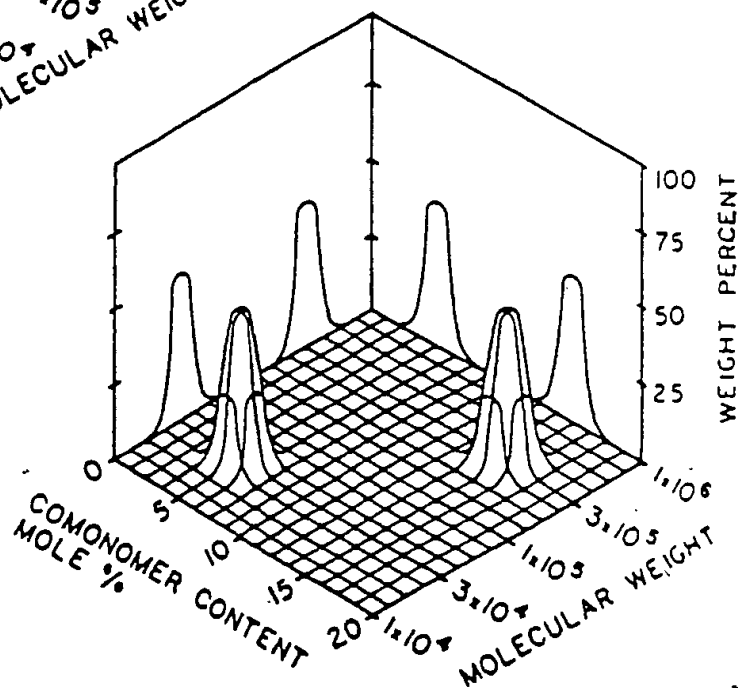
FIG. 1
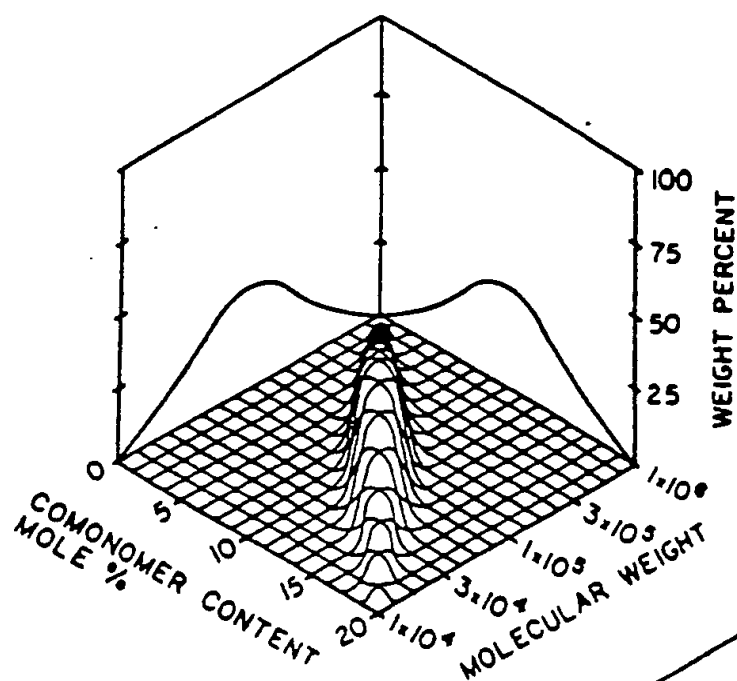
FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/04259

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 08 L 23/08

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System	Classification Symbols
IPC5	C 08 L

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP, A1, 0100843 (PHILIPS PETROLEUM COMPANY) 22 February 1984, see the whole document	1-26
A	EP, A2, 0168928 (BCL LIMITED) 22 January 1986, see the whole document	1-26
A	EP, A2, 0241234 (EXXON CHEMICAL PATENTS INC.) 14 October 1987, see the whole document	1-26
A	GB, A, 2077273 (NIPPON OIL COMPANY, LIMITED) 16 December 1981, see the whole document	1-26

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
21st December 1989	0 8. 01. 90

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	T.K. WILLIS

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	GB, A, 2148906 (OWENS-ILLINOIS INC (USA-DELAWARE)) 5 June 1985, see the whole document	1-26

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on   08/11/89
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